CrossMark

Tracing nitrogen cycling in mining waters using stable nitrogen isotope analysis

Lino Nilsson[*], Anders Widerlund

Division of Geosciences and Environmental Engineering, Luleå University of Technology, SE-971 87 Luleå, Sweden

ARTICLE INFO

ABSTRACT

We show how we used stable nitrogen and oxygen isotopes in ammonium and nitrate to identify and quantify nitrogen transformation and nitrogen sources at the LKAB mining site in northern Sweden. Stable nitrogen isotope analysis worked as an excellent tool for tracing nitrogen cycling in rapidly moving process waters. The isotope analysis was performed on the mining process waters at seven different key points along the water flow and we identified nitrification, ammonia volatilisation, and ammonium adsorption as nitrogen transformation processes. The source of nitrogen is historically explained as undetonated ammonium-nitrate based explosives. We used nitrate nitrogen and oxygen isotopes to quantify four nitrogen sources in the accumulated water in the mine as well as three sources in an above ground process water reservoir. The nitrate isotope data showed that most of the nitrate (70–80%) in the accumulated water underground originated from a sampling point located close to the surface and only a minor fraction (5–20%) originated directly from undetonated explosives (direct dissolution of NH_4NO_3 and nitrification of NH_4). Nitrate from natural groundwater formed roughly 12% of mine water nitrate. In the above ground process water reservoir isotope data indicated another source of nitrogen coming from undetonated explosives.

© 2017 Elsevier Ltd. All rights reserved.

1. Introduction

High nitrogen discharges from mine sites have been known for over a decade and has been the subject of several studies (Mattila et al., 2007, Morin and Hutt, 2009; Chlot et al., 2013, Herbert et al., 2014). The immediate environmental effects have been studied in detail, for instance by Chlot et al. (2013), who showed that nitrogen rich mining effluents caused eutrophication in receiving waters. The source of nitrogen in mine waters has been reported to be the ammonium nitrate based explosives used in blasting operations. Ammonium nitrate is easily dissolved in infiltrating groundwater and the major source is reported to be from undetonated explosives (VTT, 2015). Although the molar ammonium:nitrate ratio in the explosives is close to 1:1, the ammonium:nitrate ratio in mine process waters is usually considerably lower due to processes such as nitrification, ammonia volatilization, and ammonium adsorption. The biogeochemical nitrogen transforming processes that occur at mine sites are complex and poorly known, although the basic processes are in principle similar to those occurring in natural systems (Robertson and Groffman, 2007).

Isotope analysis has been used previously to trace nitrogen cycling processes (Kendall, 1998), and Aravena et al. (1993) used stable isotopes of nitrogen and oxygen in nitrate to identify nitrogen originating from septic systems in groundwater. Stable isotope data has also been used in systems receiving mining affected waters. For example, Chlot et al. (2015) used stable nitrogen isotopes to trace assimilation of nitrogen compounds in macrophytes, and Widerlund et al. (2014) used stable carbon and nitrogen isotopes to reconstruct historical changes in organic matter accumulation in lakes receiving nutrient-rich mine waters. Although isotope analysis is a tool for tracing and identifying nitrogen sources and transformation processes, the focus has seldom been on mine water – process water systems. The main idea behind nitrogen isotope analysis is that processes affecting nitrogen concentrations change the isotopic composition of the residual nitrogen.

The hypothesis of this study is that stable isotope data can be

* Corresponding author.
  E-mail address: Lino.Nilsson@LTU.se (L. Nilsson).

used to trace biogeochemical transformations and various sources of nitrogen in mine waters also within mines and associated processing plants. The study was carried out as a pilot-study at the Kiruna iron mine in northern Sweden, with the objective to investigate if stable nitrogen and oxygen isotope data can be used to identify biogeochemical nitrogen transforming reactions and various nitrogen sources, both in the mine as well as in the processing plants. Water samples were collected in the Kiruna mine and the associated processing plants for determination of ammonium, nitrate and dissolved oxygen concentrations, nitrogen isotope composition of ammonium and nitrate, oxygen isotope composition of water and nitrate, as well as the tritium activity in the mine water.

2. Study site

2.1. The Kiruna mine

The LKAB (Luossavaara Kiirunavaara AB) mine in Kiruna is located in the sub-arctic northern part of Sweden (lat. 67° 50.9'; long. 20° 11.7', Fig. 1) with an annual average temperature of −2 °C (SMHI, 2016). The landscape is dominated by mountains, Kirunavaara being the highest mountain in the local area (733 m a.s.l). The vegetation in the catchment area is dominated by peatland and deciduous forest (Fig. 1).

The LKAB Kiruna mine is the largest underground iron mine in the world, with an annual ore production of 25.3 million tons (LKAB, 2017). The ore is mined using sublevel caving, where the crushed ore and waste rock is hoisted to the surface. Ammonium-nitrate-based explosives with an $NH_4:NO_3$ ratio of ~1:1 used in blasting operations are the major source of nitrogen at the mine site (Chlot et al., 2013). The explosive used is an emulsion type explosive with 60—70% ammonium-nitrate addition as oxidiser (Klippmark, 2015). Approximately 20—30 tonnes of explosives are used each day at the Kiruna mine.

The mined ore is transported from the underground mine to the processing plants located on the surface. Water accumulated in the mine is transported via a pumping system up to the processing plants and then discharged to a tailings pond and a clarification pond (Fig. 1). The water is close to fully oxygenated (91—107% saturation) and the pH is weakly alkaline (pH 8—8.5).

2.2. Nitrogen input and pathways

With the sublevel caving method used in the mine, boreholes are loaded with explosives months before the charges are detonated. During this time some of the explosives can dissolve in infiltrating groundwater, and subsequently enter the mine and process water flow in the form of dissolved ammonium and nitrate. In addition, ammonium and nitrate are most likely also leached from waste rock stored on the surface (Fig. 2). This nitrogen is transported to the surface either as adsorbed ammonium on waste rock surfaces or as adsorbed ammonium-nitrate. At detonations mostly nitrous oxides gases are produced, but only $NO_2(g)$ is soluble in water. Forsberg and Åkerlund (1999) estimated the total addition of nitrogen from successful detonations to around 0.3 mg l^{-1}.

The Geological Survey of Sweden has measured nitrogen species in groundwater in northern Sweden since the mid-1970s. The closest sampling point is located roughly 40 km south-east of Kiruna and shows values between 1.5 and 2.1 mg l^{-1} NO3-N (n = 74). Another sampling station located 78.5 km north west of Kiruna in the Abisko National Park has an average nitrate concentration of 1.51 mg/l (n = 300). It's reasonable to believe that the natural groundwater NO3-N average concentration at Kiruna is around 1.5—2 mg l^{-1}.

The concentrations of ammonium and nitrate change with the flow of process water from the mine, through the mineral processing plants and into the tailings and clarification pond system (Fig. 2). However, the nitrogen transforming processes in the mine—pond system are poorly known. Processes such as ammonia volatilization, nitrification, and denitrification are likely to occur, the latter in anoxic pond sediments. It is also likely that nitrogen (mainly as dissolved nitrate) is leaching into the mine from waste rock piles (Fig. 2). All these processes will affect the isotopic composition of the nitrogen in the water.
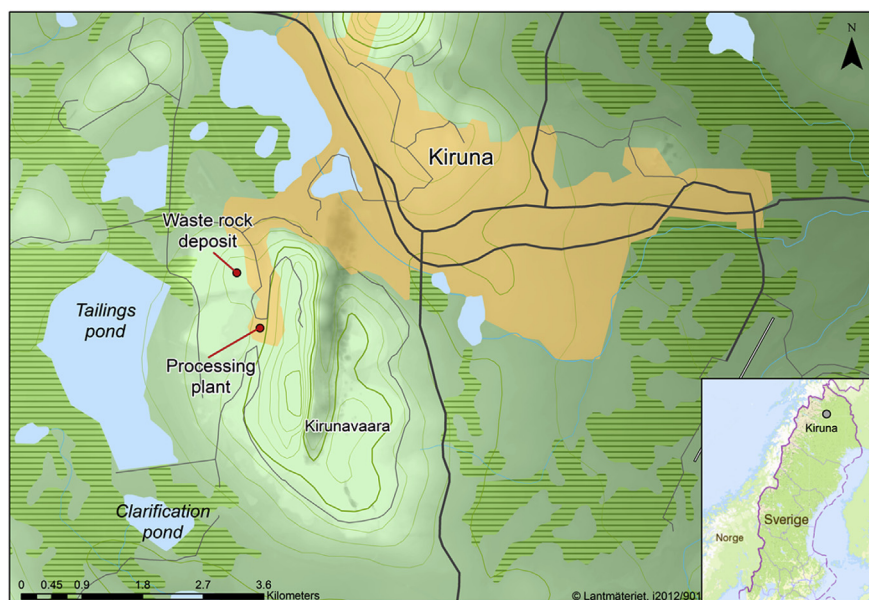

Fig. 1. Location of the Kiruna mine in northern Sweden. Hatched green is peat land, and solid green is dominated by deciduous forest. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)